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# Chapter

# Pollution Issues in Coastal Lagoons in the Gulf of Mexico

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### **Abstract**

The coastline of the Mexican Gulf of Mexico is an area of paramount importance. It poses valuable biological and ecological resources such as coastal lagoons, rivers, estuaries, wetlands and swamps. It poses 206 coastal systems including 73 coastal lagoons with high biological richness. Their study shows the physicochemical characteristics and pollution levels into the four more productive lagoons of Tampamachoco, Mandinga, Alvarado in the Veracruz state and Terminos Lagoon in Campeche state, México, have the present characteristics. The lagoons show a wide interval in physiochemical parameters (temperature: 18–32°C, salinity: 11–38 ups, and nutrients: oxygen 1.8–9.0 mg/L, total phosphorus 2.6–123 μM total nitrogen 5–70 μM, and chlorophyll 10–50 mg/m<sup>3</sup>). All of them oscillated between normal to eutrophication condition. The presence of PAHs and some of the high toxicity as anthracene, and chrysene, as well as naphthalene and its methyl derivatives has been reported. Also, chlorinated hydrocarbons used for agriculture purposes and malaria control (DDT, lindane, endosulfan) have been identified in these lagoons. Metals as Cr, Pb, Ni, Cd, and V among others were recently reported in the lagoons considered in this study. Concentrations of pollutants also show significant variations depending on the time and the type of lagoon, or estuary.

**Keywords:** Gulf of Mexico, coastal lagoons, physicochemical features, pollution, metals, petroleum hydrocarbons, pesticides, sediments, ecotoxicology, nutrients

#### 1. Introduction

# 1.1 Main coastal lagoons in the Gulf of Mexico

One of the great problems of the coastal zone of the Gulf of Mexico is the diverse and significant water load of the different anthropogenic activities which have not taken into account the volume that must be conserved for the ecological services for which have been lost atmospheres of diverse biological wealth. The coastal flood plains in the Gulf, associated with coastal zones on the border with the terrestrial zone and the sea, are subject to flooding by rainfall, excess fluvial contribution that makeup dikes and channels but that play important roles in the coastal landscape and they contribute to the high production of the coastal zone, however; they run the risk of various deteriorations with or without recovery [1–6].

The coastal zone associated with rivers, is interconnected by an extensive network of wetlands and floodplains temporary and perennial that allow the retention of water,



**Figure 1.**Location of main coastal lagoons in the Gulf of Mexico.

act as filters, deposits and source for various substances and re the habitat of plant species adapted to these conditions and fauna associated with this vegetation both emerging and submerged. The main problems that lagoons located within or near urban areas have are eutrophication, siltation caused almost always by inadequate management of the urban basin and lack of control of wastewater inlets, but in particular agriculture refuses [7–9]. The Gulf of Mexico is the ninth largest body of water in the world, with five Mexican states to the west. Due to its physical and chemical characteristics, it is a very diverse internal sea as a result of its latitudinal location; from tropical, subtropical to temperate, with climates classified as "dry" (spring), rainy (summer, autumn) and northern (winter) [10]. The coastal lagoons and estuaries of the Gulf of Mexico have been characterized environmentally taking into account: their location, shape, size, runoff and tributary streams, number and size of the mouths of connection with the sea, their behavior throughout the year, their bathymetry, internal currents, the type of sediment they receive from the watershed to which they are associated, gases, dissolved solids or salinity and primary productivity, among others [11]. Based on the foregoing, each coastal lagoon and estuary differs in their mentioned characteristics. Given the high number of coastal systems of the Gulf, the present work has the objective of choosing four coastal lagoons (**Figure 1**) to exemplify their physicochemical natural variations in space and time considering their geographic location two; as well as the level metals, hydrocarbons, and pesticides. This chapter is comprised: a brief description of a four coastal lagoon of the Gulf of Mexico chosen in this study, as well as of the incorporation of previously published information with the methods used to obtain data; the presentation of the results and the consequent discussion; and brief comparison with other lagoons of the coastal region; and the most outstanding conclusion.

#### 2. Methods

## 2.1 Metals

The technique used for metals was that described [12] consisting of a digestion in a microwave oven (CEM Mars5x) with 3 mL of HF, 10 mL of reagent water and 5 mL

of super-pure  $HNO_3$ . The samples were read in an ICP-MS (ICP 7500c). Analytical quality was controlled using approved standards, reference material certified for marine sediments (IAE-433). The methodologies used for the analysis of metals are based mainly on the use of acid digestion in a microwave, obtaining afterward the concentrations in an Atomic Absorption Spectrophotometer or in ICP-MS.

# 2.2 Petroleum (PAHs)

The samples were analyzed for the 16 priority PAHs [13] following the method recommended [14] and used worldwide in marine pollution studies [15–17]. This method involves an organic extraction with n-hexane: methylene chloride 50:50 v/v, concentration of the extract, clean-up using a silica pack, aluminium oxide and anhydrous sodium sulfate, eluted with n-hexane mixtures: methylene chloride 80:20 and 50:50 to obtain the aromatic fraction; the samples were concentrated under a soft  $N_2$  current to dryness.

# 2.3 Organochlorine pesticides (OCs)

The OCs included the HCH (alpha, beta, gamma and delta isomers), DDT and its metabolites (p,p'-DDT, p,p'-DDD and p,p'-DDE) and the cyclodiene group (heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, endrin aldehyde, endosulfan I, endosulfan II and endosulfan sulfate); the  $\Sigma$ OCPs was calculated from the sum of 16 organochlorine pesticides mentioned. The sediment samples were processed following the technique proposed [18] reported in several studies [19–22]. It consists of extraction with HPLC grade n-hexane, concentration of the organic extract, and cleanup by adsorption chromatography using Florisil and anhydrous sodium sulfate. The cleanup column was eluted with the mixtures n-hexane:ethylic ether 9:1 and 8:2; the final solution was concentrated with N<sub>2</sub> to 2–3 mL for GC analysis. All organic pollutants (PAHs and OCs) were quantified using a Hewlett–Packard 5890 series II gas chromatograph (GC) equipped with an HP-5 silica fused capillary column (30 m × 0.25 mm i.d. with 0.25  $\mu$ m film thickness).

A flame ionization detector (FID) and an electron capture detector (ECD) were used for PAHs and the organochlorine compounds, respectively. Quantification was carried out using the internal calibration method based on a five-point calibration curve for individual components. The percentage of recovery of PAHs and OCs ranged from 85 to 105%. For each batch of 10 samples, a procedural blank, a spiked blank and reference standard material were processed (IAEA-417). Detection limits (DLs) were  $0.01 \, \mu g \, g^{-1}$  for PAHs and  $0.01 \, ng \, g^{-1}$  for OCs.

#### 3. Results

#### 3.1 Physicochemical composition

# 3.1.1 Tampamachoco lagoon system (TLS)

Tampamachoco lagoon system (TLS) is located in the Coastal Plain of the Gulf of Mexico, in the state of Veracruz, between the parallels 20°58′ 15″–21°05″ N and the meridians 97°20′ 30″–97 24″ W [23]. It is formed by the Tampamachoco lagoon (1500 ha), occupying a total area of 6870 ha. The climate is of the "Aw type 2" (e) that is to say warm subhumid with rain in the summer [24], with an annual rainfall of 1900 mm, being January the driest month and September the

rainiest. Is a shallow system with an average depth of one-meter, high turbidity [25] and only discharges to the south the river called Tuxpan near the marine mouth, through which it communicates with the Gulf of Mexico [26, 27]. Total nitrogen and total phosphorus are high, which represent the anthropogenic influence (**Table 1**).

# 3.1.2 Mandinga lagoon system (MLS)

Mandinga lagoon system (MLS) is located between 19°00′ and 19°06′ N and 6°02′ and 96°06′ W. It has a complex morphological conformation constituted by three lagoon bodies; it has an extension of 3250 ha [9]; these. Receives several affluent of other less important rivers [28]. The type of climate in the MLS is Aw2 (w) (i) W "with average rainfall of 1676 mm/year and average evaporation of 1500 mm/year [28]. The temperature has an interval between 25 and 31°C approximately similar to that of the bottom, according to the geomorphology and the annual climate (rains and drought) (**Figure 1**). This lagoon has a high chlorophyll that represented high primary production (**Table 1**).

# 3.1.3 Alvarado lagoon system (ALS)

Alvarado lagoon system (ALS) is located in the South Coastal Plain of the Gulf of Mexico, between the coordinates 18°44′00″ and 18°52′15″ of latitude N and 95°44′00" and 95°57′00" of longitude W (Figure 1). This lagoon system leads to several rivers within the most important is Papaloapan, and it is made up of several internal (7162 ha), the type of climate is subhumid warm (Aw2), with little thermal oscillation. According to INEGI (National Institute of Statistic and Geography) [29], the climate is warm-sub-humid-the wettest of the sub-humidwith rain in summer. The dry season occurs between the months of January to May, the rainy season begins in June and the north winds season which are cold wind masses. In addition, this water body is affected by depressions, tropical storms, and hurricanes. The main river basin is the Papaloapan River, which has a complex system of wetlands and borders on its active agricultural activity. The ALS, is considered the third largest wetland in Mexico (National Commission of Biodiversity) [30, 31], it is also one of the most productive systems of the Gulf of Mexico [32] and a shelter area for the feeding and reproduction of numerous populations of fish and crustaceans [33]. The region where this lagoon is located presents several environmental problems: change in land use such as road construction, landfills, agriculture; also the mangrove felling and modification of the vegetation; the use of biocides (organochlorine, organophosphorus), discharge of urban and industrial waters such as sugar, paper and even urban wastewater from cities upstream, overfishing, among others [34]. Total nitrogen, total phosphorus and ammonium are so high (**Table 1**).

#### 3.1.4 Terminos lagoon system (TELS)

Terminos lagoon system (TELS) is considered the largest coastal estuary in Mexico, it is located at the eastern end of the extensive and complex delta of the Usumacinta River that extends approximately 125 km along the southern coast of the Gulf of Mexico, with an average depth of 3.5 m. The TELS lies between 91°10′ and 92°00′ W longitude and parallels 18°20′ and 19°00′ N latitude, in the state of Campeche. Had two marine mouths that communicate it permanently with the Gulf of Mexico [25]. The lagoon receives large volumes of fresh water that vary according to the climatic epochs in a 49,700 km² basin. It also receives water from

			Phys				
Area	Salinity Temper	ature Dissolved oxygen	Total nitrogen	Total phosphorus	Ammonium	Orthophosphates	Chlorophyll "a"
	ups °C	mg/L	$\mu M$	$\mu { m M}$	$\mu M$	μМ	mg/m <sup>3</sup>
Tampamachoco lagoon system (TLS)	11–38 18–3	32 0.3–9	5–71	2.6–123	1–35	0–89	2–14
Mandinga lagoon system (TLS)	8–32 28–3	33 4–6	5–17	5–10	2–10	0.2–2	10–52
Alvarado lagoon system	0.3–34 25–3	31 10–18	36–429	17–41	15–25	0.4-6	22–49
Terminos lagoon system (TELS)	28–34 26–3	3–10	2–30 inorg.		4–26	0.1–7	3–20
Yucateco lagoon, Tabasco state	0.5–33 21–3	35 0.5–8	7–228	3–138	0.5–31	0.5–18	jul-28
Mecoacan lagoon, Tabasco state	1–14 24–3	30 3–5	29.41		5–14	0.4–4	7–21

**Table 1.** *Physicochemical composition.* 

the Yucatan Peninsula, the lowlands of Tabasco and the highlands of Chiapas and Guatemala [35]. Three main rivers discharge their waters to the lagoon. The type of climate is warm sub-humid Amw [36] isothermal, with a rainy season from June to October, Northwinds from November to March and a dry season from April to June. It is influenced by extraordinary natural processes such as northerly and tropical storms and hurricanes [37]. The margins of the lagoon are covered by mangroves with a predominance of *Rhizophora mangle*, *Avicennia germinans* and *Laguncularia racemosa* [38, 39] and the seagrass *Thalassia testudinum* (**Figure 1**). Total nitrogen and ammonium are high (**Table 1**).

#### 3.2 Pollutants

3.2.1 Petroleum (PAHs)

Oil pollution and its derivatives are considered to be one of the biggest environmental problems in the Gulf of Mexico [40] and in its waters have been occurred the two largest oil spills at the sea, such as: the Ixtoc-1 well in the Campeche Sound and that of the Deepwater Horizon, off the coast of Louisiana, USA. Both affected significantly the diverse ecosystems of the coastal areas. Thus and in spite of the fact that the Mexican coastal lagoons settled on the margins of Veracruz, Tabasco, and Campeche, are highly productive and of high economic value. Analysis of petroleum hydrocarbons conducted in these lagoons showed important concentrations of aromatic hydrocarbons originating from the intense oil activities that develop along their coasts. In the present contribution, the updated available information on the levels of concentration of PAHs in sediments of the lagoons of Tampamachoco, Mandinga, Alvarado in the state of Veracruz and one of Terminos in Campeche is gathered. In the cases of the lagoons of Tampamachoco and Alvarado also sedimentary nuclei analysis were carried out, which give us a historical view of these pollutants for approximately 80 years old and in the same way the tendency in time that have these compounds.

#### 3.2.1.1 TLS

The sediments of the TLS and the Tuxpan River, Veracruz, were evaluated during the end of July 2012. From the results of the 16 priority PAHs determined, the greater (1.30  $\mu$ g g<sup>-1</sup>  $\Sigma$ HAPs) was registered in the station located in front of the Thermoelectric Power Plant (CTPALM) and the minimum  $(0.02 \,\mu g \,g^{-1})$  in site located in the north of the lagoon body. The analysis of a sedimentary core [7] in the TLS showed an average concentration of PAHs of the nucleus of 0.98  $\pm$  0.38  $\mu$ g g<sup>-1</sup>. When analyzing the vertical distribution of the PAHs content, it was found that the historical pattern showed an increase from the basal level of the  $\Sigma$ PAHs of  $0.29~\mu g~g^{-1}$  at the beginning of the last century (1908), until reaching the maximum of 1.79  $\mu g \ g^{-1}$  in 1999, and decrease towards the beginning of the twenty-first century in 0.58  $\mu g$  g<sup>-1</sup> (2003) to show a new increase in 2010 with 0.84  $\mu g$  g<sup>-1</sup>. The compounds with the highest concentrations were, dibenzo[ah]anthracene (0.28  $\mu$ g g<sup>-1</sup>), in order of decreasing followed fluorene (0.13  $\mu g g^{-1}$ ) and benzo[a]anthracene  $(0.12 \,\mu g \, g^{-1})$ . The molecular profile in the eight analyzed strata, changed, of petrogenic origin in 1908, to be dominated by pyrolytic compounds and to a lesser extent by petrogenic from 1999 to the present time. It should be noted that the individual concentrations of PAHs in sediments were lower than the international sedimentary quality criterion (**Figure 3**), with less probability of causing adverse effects to the benthic community. Thus, it can be said that there is no risk derived from the intrinsic toxicity of the coastal sediments analyzed from this group of hydrocarbons.

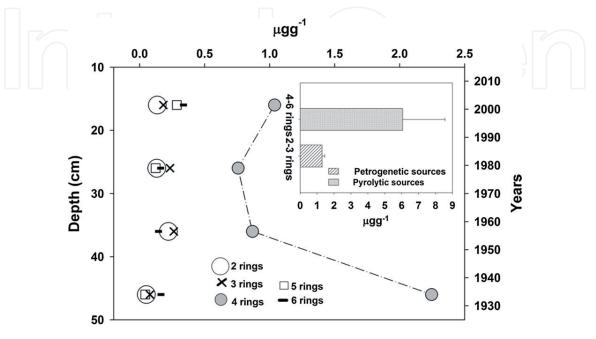
From the analysis of individual PAHs, it can be seen that the predominance of compounds with 3–4 rings indicates inputs of pyrolytic and petrogenic hydrocarbons from human activities around the lagoon.

#### 3.2.1.2 MLS

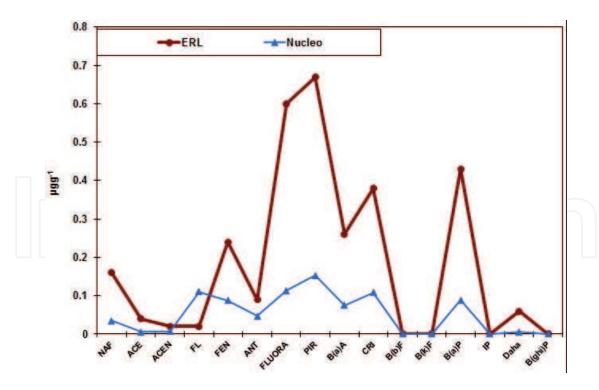
In **MLS** was in which the highest values of PAHs were determined with a range of  $2.2–18.2~\mu g~g^{-1}$  (average  $5.68~\mu g~g^{-1}$ ). The compounds that stood out were chrysene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[a]anthracene, all of them considered of environmental concern. This lagoon receive directly the urban discharges of settlements south of the Port of Veracruz and refuses from steel and iron plant placed in its nearby.

#### 3.2.1.3 ALS

The analysis conducted in a sediment core into ALS did not show a tendency to increase over time, possibly due to the source types of those compounds. The average sum of the 16 PAHs analyzed in the four strata was 1.84  $\pm$  0.54  $\mu$ g g<sup>-1</sup>, which indicates a downtrend from the year 1929 to 1971 (with values from 1.5 to 1.3  $\mu$ g g<sup>-1</sup>), and a slight increase near the superficial stratum corresponding to the year 1998 (about 2.0  $\mu g g^{-1}$ ). These values are far below the ERL index of  $4.02 \,\mu g \, g^{-1}$ . The compound with the highest value in all core strata was chrysene, except for the stratum from 26 to 36 cm, where it was below the detection limit; the highest concentration in this stratum corresponded to  $benzo[\alpha]$  anthracene with  $0.591 \,\mu g \, g^{-1}$ , benzo [ $\kappa$ ] fluoranthene and indeno [1,2,3,c,d] pyrene compounds were not detected by the analytical method employed for their determination [41]; only the latter showed a concentration of  $0.0427 \,\mu g \,g^{-1}$  in the deepest stratum corresponding to the year 1929. This study showed that compounds with four aromatic rings were predominant in all core strata (Figure 2), which suggests that they were byproducts of pyrolytic processes near the study zone, such as high-temperature combustion of organic matter and fossil fuels. The sum of the four-ring PAHs presented practically the same collective tendency as the sum of the 16 quantified PAHs. This indicates that the contribution to the entire historical profile of both



**Figure 2.** ALS core concentrations of PAHs ( $\mu g g^{-1}$ ) based on number of aromatic rings.



**Figure 3.** Individual PAHs and ERL sedimentary quality criteria in the sedimentary core of TLS.

five and six-ring PAHs, as well as two and three-ring ones (which originate from petrogenic sources associated to drilling activities, such as oil extraction and oil spills), was minor (**Figure 2**).

Most of the PAHs in the sediments proceed from pyrolytic sources, while the sources of compounds consisting of two and three rings are of petrogenic origin. The total PAHs sum was mostly contributed to by compounds consisting of four benzene rings, namely chrysene. Despite slightly higher than ERL index concentrations for anthracene, acenaphthylene, fluorene and dibenzo  $[\alpha,h]$  anthracene, the total PAH sum did not exceed that limit. It has to be pointed that human activities are very intense in the lagoon as fisheries, shipping port, storage of petroleum and agriculture.

#### 3.2.1.4 TELS

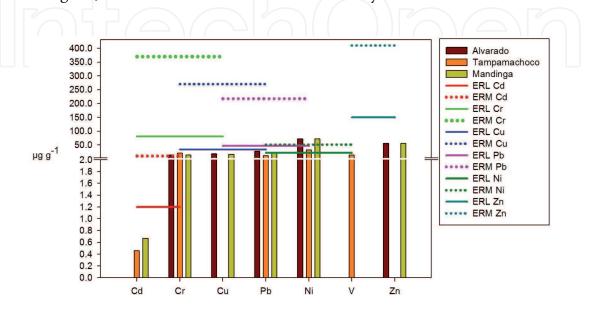
On the other hand, TELS has been intensively studied for organic and inorganic pollutants due to its importance as a fisheries center. Thus, Ref. [42] indicates the presence of PAHs in sediments and oysters of this lagoon, reported PAHs in oyster tissue and the predominance of alkylated compounds of medium and low molecular weight indicating a petrogenic origin attributed basically to off-shore oil activities. This lagoon it is located in front of the main oil wells in the Bank of Campeche were the most intense exploration and exploitation of crude oil takes place.

Another study of PAHs performed on fish tissue from the western zone of TELS, showed that its concentrations exceeded the values maximum recommended by international regulation (greater than 40.0  $\mu g$  g<sup>-1</sup>) for the *Petenia splendida* cichlid fish [1]. In recent years [2] evaluated dissolved PAHs and mention that in Boca del Carmen, were determined high concentrations of PAHs; as well as a bacterial community that degrades very abundant PAHs. This is a clear indication that the lagoon arrive at all times dissolved/dispersed PAHs from oil activities carried out in the Sonda de Campeche.

#### 3.2.2 Metals

The investigations on metals in sediments that have been carried out in three of the main coastal lagoons of the Veracruz state, show significant results: the Cd registered similar concentrations for the TLS and MLS with values of 0.46 and  $0.66 \,\mu g \, g^{-1}$  respectively, and these values were below the ERL that is 1.2  $\mu g \, g^{-1}$ , levels that produce adverse biological effects in sediments [43]. On the other hand, the highest concentration of Cr was for the TLS with 20.52  $\mu$ g g<sup>-1</sup>, the concentrations for ALS and MLS registered similar values with 13  $\mu g \, g^{-1}$ . The concentrations for the three lagoons were below the limit of the ERL which is 81  $\mu$ g g<sup>-1</sup>. The Cu values for MLS and ALS were 15.77 and 17.49  $\mu g g^{-1}$  respectively. These also stayed below the ERL which is 34  $\mu g$  g<sup>-1</sup>. The Pb showed values for MLS and ALS of 23.37 and 27.49  $\mu$ g g<sup>-1</sup>, while for TLS they recorded lower values (11.42  $\mu$ g g<sup>-1</sup>). The concentrations of this metal in the three lagoons remained below the ERL which is 46.7  $\mu$ g g<sup>-1</sup>. They report that Zn showed similar values for ALS and MLS with 55.81 and 56.14  $\mu$ g g<sup>-1</sup> respectively, and their concentrations were below the ERL which is 150  $\mu$ g g<sup>-1</sup>. The Ni was presented with values of 71.80 and 72.26  $\mu$ g g<sup>-1</sup> in the lagoons of ALS and MLS respectively, and which are above the ERL which is 20.9  $\mu g g^{-1}$ . The enrichment of Ni in the surface sedimentary substrate is due to the contribution of urban discharges from urban discharges and industries that are close to the coastal areas where the present study was conducted (**Figure 4**) [1, 44].

Villanueva and Ramirez [6] carried out the determination of Cd, Cr, Ni, Pb and V in sediments of the TLS, collected in seven stations. The concentrations decreased in the following order Cr > Ni > Pb > V > Cd, where the latter has not increased since 2010. Although Cd and Pb did increase in 2012, the determined values did not exceed the ecological criteria of the minimum and maximum adverse conditions for the biota (ERL and ERM), while the levels of Ni decreased compared to 2010, since they have a direct influence of the terrestrial and riparian drainages, which present higher hydrodynamics and a greater mixture due to the salt wedge coming from the sea. Likewise, there were no specific changes in metal concentrations between the years 1985 and 1988, the period in which the Thermoelectric Power Plant was built and started to operate. In the period from 1996 to 2012, the concentrations of Cd, Cr and Pb showed slight increases, while the Ni showed variation. Similarly, Vazquez-Botello et al. [23] performed the analysis of a sedimentary core in this lagoon, which concludes that there is a tendency to increase from the oldest



**Figure 4.**Average concentrations of metals in superficial sediments of coastal lagoons of the Veracruz state.

stratum (1908) with surface maximums, the values of Ni and Pb are below the concentrations reported in Literature for other coastal and lacustrine systems. The basal values of Cd (0.22  $\mu g \, g^{-1}$ ), Cr (31  $\mu g \, g^{-1}$ ), Ni (26  $\mu g \, g^{-1}$ ) and Pb (12  $\mu g \, g^{-1}$ ) were also determined. From previous reports, becomes clear that the atmospheric transport is one of the main sources of Pb towards the lagoons, rivers, and oceans; and this is reflected in its levels in the sediments of the lagoons studied. For which it is recommended to analyze sedimentary nuclei and determine the origin of it. Also, the Ni detected in the studied lagoons, has a mixed origin: one part is of lithological origin and another part from the urban discharges through the particulate solids, as well as through the use of fertilizers and the mining industry and steel, and whose concentration surpasses the ELR and ERM values proposed by Long et al. [43] to the up to 100%, causing enrichment of the sedimentary substrate analyzed.

# 3.2.3 Organochlorine pesticides (OC)

The data for organochlorine pesticides (OC) are presented in sediments of the lagoon systems considered in this study. The TLS has records of these agrotoxics of three practically continuous annual cycles (2009, 2010 and 2012), while the remaining ecosystem data correspond to a particular year; the values are given in ng  $g^{-1}$ dry weight. **Figure 5** shows the total data of the OC ( $\Sigma$ OC) reported in sediments of these coastal lagoons. For ALS the sediments evaluated in 2009 occupy the first place with a value of 36.2 ng  $g^{-1}$  [3] while in lower concentrations were TLS in the same year with 13.3 ng g<sup>-1</sup> decreasing to 4 ng g<sup>-1</sup> in 2012 and the lowest total concentration of organochlorines was for the TELS with 0.18 ng  $g^{-1}$  [4]. This marked difference between lagoon systems in the same coastal region of Mexico may be due to the local uses of these agrochemicals, as well as to the particular conditions of temporary runoff and large permanent flows and to the human activities carried out in the nearby of these ecosystems. The area of continental influence of the ALS has a great agricultural activity mainly due to the sugarcane plantations and its main tributaries, the Blanco and Papaloapan rivers, that cross several hundred kilometers of cultivation areas ending in this lagoon. Thus, the suspended material with large amounts of organic matter and a high probability of carrying adsorbed pesticides are finally stored in the lagoon sediments. On the other hand, the hydrodynamics of the TLS is contrasted since human activity in this area is more urban and industrial, and applying pesticides as vector control and to a lesser extent to the agricultural use. The TELS in the south of the GoM, has greater dimensions and a great interaction with the GoM in the replacement of its body of water, as well as a more estuarine environment due to the mixture with tributaries of the flow fluvial Grijalva-Usumacinta

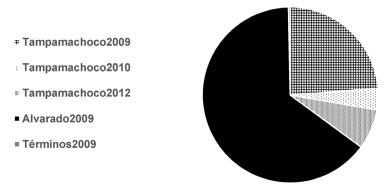
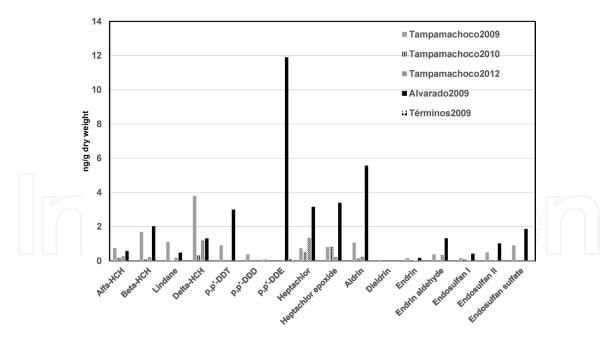


Figure 5.

Total concentration of organochlorine pesticides ( $\Sigma$ OC) in coastal lagoon sediments of three Mexican systems, Tampamachoco, Alvarado and Terminos in the Gulf of Mexico. Values in ng  $g^{-1}$  dry weight.



**Figure 6.** Individual pattern of organochlorine pesticides in coastal lagoon sediments of three Mexican systems, Tampamachoco, Alvarado and Terminos in the Gulf of Mexico. Values in  $ng g^{-1}$  dry weight.

which can contribute with materials and energy to the lagoon system and likewise export to the GoM what can explain the low concentration of reported OC.

The diversity of OC reported for these three Mexican lagoon systems is presented in **Figure 6**, where 16 representative compounds of the three major chemical families were registered: alicyclic or Lindane group, aromatics or conglomerate of DDT and cyclodienes the most diverse group that includes the "Drines," Heptachlor and Endosulfan. The highest data corresponded to the ALS, the p,p'-DDE was the pesticide with the highest concentration with 11.9 ng g<sup>-1</sup> and from this same group there was record of p,p'-DDT in these sediments of ALS with 3 ng g<sup>-1</sup> what shows until that date of an old use of the insecticide. From the Lindane family, the delta-HCH isomer was found at a higher level in the TLS sediments of 2009 with a value of 3.8 ng  $g^{-1}$  and beta-HCH in ALS of 2 ng  $g^{-1}$ , which highlights the fact that application of this commercial tick due to the persistence of these isomers as a geochemical trace of its use on all livestock. Of the cyclodienes, there were records of a wide variety, in ALS were present Heptachlor and its epoxide and it was worrying the concentration found of Aldrin with 5 ng  $g^{-1}$  since it is a pesticide banned in Mexico since 1991 [45]; this same pesticide although to a lesser degree was also registered in TLS and in TELS, which shows the persistence of this organochlorine and probably recent illegal uses since in the ALS it was higher than that found in Dieldrin and Endrin. Endosulfan and its sulfate form were also recorded in the sediments analyzed in this study, without showing a clear trend; however, an incipient pattern in the degradation of the commercial mixture of Endosulfan can be seen due to a higher level of sulfate in the three lagoon ecosystems.

Because there are no maximum permissible limits for OC in coastal sediments in Mexico, it is important to consider the international sedimentary quality criteria that environmental agencies such as the NOAA of the United States of America have as the reference [46]. In this sense, the concentrations reported for lindane or the gamma-HCH isomer were higher than the threshold concentration or TEL by its acronym in English, of 0.32 ng g $^{-1}$  to cause adverse effects to estuarine benthos for the coastal system TLS of 2009 and ALS of the same year and also in the first case was also greater than the criterion of probable alteration known as PEL of 0.99 ng g $^{-1}$ , so it can be considered a scenario of real anthropogenic environmental

alteration and of potential risk to human health since various benthic organisms of these coastal sites are for food consumption [47]. Another similar case is that which occurs for *p,p'*-DDT since in the sediments of the ALS, it exceeded the biological damage threshold established in 1.19 ng/gas well as a second ecotoxicological criterion, the ERL was known as the level of effect low by its acronym in English that has a value of 1 ng g<sup>-1</sup>; of this aromatic family, the p,p'-DDE reported in this analysis was much higher than the environmental references TEL and ERL, that is, 2.07 and 2.2 ng  $g^{-1}$  respectively for what was reported in ALS, as has already been described, means that, in spite of the biogeochemical transformation of p,p'-DDT in p,p'-DDE, the benthic toxicity continues for this ecosystem that harbors several species of edible mollusks such as oysters and clams. It is worth mentioning the case of Dieldrin in the context of biotic damage since, despite not having presented large concentrations in the analyzed systems, its environmental reference concentrations are very low, evidencing the danger it has for organisms since from  $0.02 \text{ ng g}^{-1}$  can cause harmful effects (ERL) so, this risk already exists initially in the TLS since 2009.

# 4. Discussion

# 4.1 Physicochemical composition

The study and protection of coastal systems, such as coastal lagoons, wetlands, and estuaries, should be a priority for countries that have benefited from an extensive coastal zone such as Mexico. However, the accelerated development and industrialization of these areas have led to processes of degradation and alteration in these important systems.

Although Mexican coastal lagoons are important sites for fishing, aquaculture, the development of communities and that provide economic resources of great value, reports on increasing levels not only in nutrients, hydrocarbons, metals and pesticides two, that appear in the literature every day and lately plastics and microplastics that impact them and put at risk environmental and human health.

The coastal system of Gulf of Mexico has different climate, morphology and complex river flow which discharges to the lagoons, resulting in wide natural physico-chemical water composition, but it must be considered the high urban settlement with their economic activities as different industry that incremented the concentration of certain chemical compounds. This is the case of inorganic nutrients that in the present work included four coastal aquatic system (Tampamachoco, Mandinga, Alvarado and Terminos lagoons), all of them with a eutrophication conditions by high total nitrogen, total phosphorus and ammonium result of urban, agriculture and others economic activities, settlement in the margin of the river and lagoons and the residual water that are dispose to this system. This situation is in a great number of many lagoon system in the Gulf of Mexico; for example: la Mancha, Farallon, El Llano and El Verde located at the north of the Gulf of Mexico, in which were register high concentration of nitrogen, phosphorus and ammonia that result in eutrophication two [40, 48].

#### 4.2 Pollutants

#### 4.2.1 Petroleum (PAHs)

The results on PAHs indicate that these compounds are widely distributed in coastal areas and are stored in lagoons, estuaries, and wetlands. There is abundant

literature on this [49] and thanks to the use of sedimentary cores we know that these pollutants have been introduced to the lagoons more than 50 years ago and that their presence can originate as waste from oil activities or by the pyrolysis such as volcanism, burning of coal, burning of pastures and forest fires. Regarding its presence, the dominant PAHs are formed by four rings (pyrolytic) such as chrysene, benzo[a]anthracene, benzo[k]fluoranthene and benzo[b]fluoranthene. In general, their concentrations do not exceed the criterion of maximum concentration to cause adverse biological effects [46].

## 4.2.2 Metals

Comparing the concentrations of metals in the sediments listed in **Table 2**, the Yucateco and Mecoacan lagoons report high levels with respect to the three lagoons considered in this study. The Cd presented up to an order of magnitude higher (1.84 and 1.46  $\mu$ g g<sup>-1</sup>), this shows that Cd has a lithological as well as anthropogenic origin. The Cr and Pb are up to 100% above the areas of this study (36.32 and 48.30  $\mu$ g g<sup>-1</sup>), while Pb has a natural origin, by atmospheric transport, as well as anthropogenic. However, the V was the one that reported the highest concentrations in the Mecoacan lagoon with 18.78  $\mu$ g g<sup>-1</sup>. What is clear is that part of the Ni and V has their origin in the composition of the dominant oil in the area. These levels can be considered normal and expected, since there are oil wells in the vicinity of the Yucateco lagoon and Mecoacan lagoon. In **Table 2**, it is clearly observed how the variations in the concentrations of the metals analyzed are influenced by the

	Pollutants									
Area	PAHs (μg g <sup>-1</sup> )	Cd (μg g <sup>-1</sup> )	Cr (μg g <sup>-1</sup> )	Cu (µg g <sup>-1</sup> )	Pb (μg g <sup>-1</sup> )	Ni (μg g <sup>-1</sup> )	$V$ ( $\mu g g^{-1}$ )	$Zn$ $(\mu g g^{-1})$	OC (ng g <sup>-1</sup> )	
Tampa- machoco lagoon system (TLS)	0.98	0.46	20.52	N.D	11.42	31.11	13.91	N.D	19.65	
Mandinga lagoon system (TLS)	5.68	0.66	13.00	15.77	23.37	72.26	N.D	56.14	NR	
Alvarado lagoon system	2.00	N.D	13.75	17.49	27.49	71.80	N.D	55.81	36.21	
Terminos lagoon system (TELS)	6.12								0.18	
Yucateco lagoon, Tabasco state	3.85	1.84	36.32		48.30	53.90	1.61		57.71	
Mecoacan, Tabasco state	0.15	1.47	28.93		21.22	58.94	18.78		5.1	

**Table 2.**Average levels of pollutants in sediments of the four lagoons analyzed.

activities carried out in each of the surrounding areas, as well as the special and temporary hydrodynamic predominant according to the different seasons of the year [50, 51].

# 4.2.3 Organochlorine pesticides (OC)

The analysis carried out to determine the presence of OC in sediments of various coastal lagoon ecosystems of the Gulf of Mexico, provides information on the anthropogenic alteration that has been occurring for several years on these sites, given the lack of vigilance on the part of the Mexican environmental authorities in order to avoid the use of banned pesticides and internationally designated as highly dangerous, so it is urgent to modify agricultural practices, and to promote the integrated management of pests that include biological control and agroecology [52]. For comparison purposes, in **Table 2**, OC data from two tropical coastal lagoons of the Gulf of Mexico were integrated, the first being El Yucateco, whose history of anthropogenic impact has been remote since 1950 at the beginning of oil exploration and exploitation. The second is Mecoacán, considered the area of greatest fishing production in this Mexican coastal region, both located in the tropical state of Tabasco. The data of the  $\Sigma$ OC recorded in the recent sediments of El Yucateco were the highest in the comparison, with a value of 57.71 ng  $g^{-1}$  and the high presence of beta-HCH one of the highly persistent isomers of Lindane as an unequivocal trace of the use commercial of this acaricide, as well as high levels of Heptachlor epoxide, records of other cyclodienes, mainly Aldrin, Endosulfan sulfate as a product of biogeochemical transformation of the commercial product Endosulfan and the whole group of DDT with higher prevalence of p,p'-DDT [53, 54]. In decreasing order, Alvarado and Tampamachoco followed with a total concentration of OC of 36.21 and 19.65 ng g<sup>-1</sup>, respectively, as already described in this chapter; Subsequently, the global data on sediments from Mecoacan lagoon was presented with 5.1 ng  $g^{-1}$  contrasting with El Yucateco and the neighboring coastal systems of southern Veracruz already mentioned; The dominant pesticides in the sediments of this Tabasco lagoon were similar to those of El Yucateco, Heptachlor epoxide and, to a lesser degree, Aldrin, Dieldrin and beta-HCH as a Lindane residue. The DDT family was not detected [55]. Finally, the Terminos lagoon presented the lowest total concentration of OC of the comparison presented in **Table 2** with 0.18 ng g<sup>-1</sup>, so it can be clearly observed the coastal sites that require greater environmental monitoring as well as the adequate application of the regulation on these xenobiotics to reduce the sedimentary load of OC to concentrations of lower or no biological risk and to avoid the ecological impact and human health given the persistence and biomagnification capacity of these agrotoxics.

# 5. Conclusions

The difference physicochemical characteristic and pollutants concentrations of analyzed in the coastal lagoons of the Gulf of Mexico are due to the biochemical behavior, climatic factors and, of course, the industrial and urban discharges that reach these lagoons over time. Other factors are the morphology of the coastal lagoons, presence of mangrove isless that can serve as traps of inorganic or organic matter and pollutants retention. In general, it is considered that urban wastewater constituted the most important source of nutrients which tendency to eutrophication in those lagoons.

This urban wastewater constitutes the most important source of metals in rivers and lagoons two. These effluents consist of (1) untreated or mechanically treated

waters only; (2) substances which have passed through filters and biological treatment plants, either solubilized or as finely divided particles; and (3) substances that are served by an emitter and that discharge to the coastal zone. The solid particles of wastewater from coastal cities cause the enrichment of metals, such as Cr, which can have high concentrations, as well as the use of chromates in petrochemical processes during oil extraction. It is worth mentioning that there are numerous studies on the role of atmospheric transport as a source of pollutants (metals, pesticides and aromatic hydrocarbons) and the one that stands out is the contribution of Pb which has been demonstrated in the ice of the North Pole and Greenland, where concentrations of 0.200 µg Pb/kg of ice [56]. The foregoing reveals the fact that the atmospheric contribution, far from being assumed insignificant, even becomes the main source of supply of some pollutants for coastal systems. However, the accelerated development of certain economic activities such as the oil industry, energy generation, tourism, agricultural development and maritime transport have led to disorderly growth in the national coastal areas, with consequent environmental conflicts arising from competition for space, the use of resources and the generation of toxic and polluting waste. Indeed, the conflicts that affect the quality of life and decrease the competitiveness of the same sectors and their economic activities.

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